

**TITLE:       USE OF PEROXYACIDS/HYDROGEN PEROXIDE FOR  
REMOVAL OF METAL COMPONENTS FROM PETROLEUM  
AND HYDROCARBON STREAMS FOR DOWNSTREAM  
5               APPLICATIONS**

**CROSS-REFERENCE TO RELATED APPLICATION**

This application claims priority under 35 U.S.C. § 119 to Provisional Application U.S. Serial No. 62/774,625, filed on December 3, 2018, which is herein incorporated by  
10 reference in its entirety including without limitation, the specification, claims, and abstract, as well as any figures, tables, or examples thereof.

**FIELD OF THE INVENTION**

The disclosure relates to the use of peroxyacid formulations, including but not  
15 limited to peracetic acid and performic acid, for enhancement of downstream processes through removal of soluble and particulate metal complexes from petroleum oils and refinery feedstocks and/or streams. This serves to minimize fouling, decrease the propensity for a solid stabilized emulsion and in turn, improve waste water quality. The methods and compositions are particularly useful for mitigation of heavy metals in  
20 petroleum oil and for offsetting potential solid loading resulting from use of a metal based H<sub>2</sub>S scavenger or other commonly applied metal-based additives. The methods and compositions are also useful for enhancing coke quality via decreased metal concentrations, reducing bacteria in slop oil and crude tanks, as well as reducing downstream catalyst poisoning.

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**BACKGROUND OF THE INVENTION**

A survey of a random selection of desalters in the United States found that a significant increase in iron concentration and filterable solids was observed at the desalter interface relative to the raw crude charge. This suggests that solids, sediment or fine  
30 particulate, are concentrating at the desalter interface and promoting emulsion stability. If not effectively managed, a decrease in the desalting efficiency of the unit may occur, in addition to other problems such as oil under-carry to the waste water treatment plant and increased slop oil generation. In addition, a number of United States refiners

processing light tight oil have reported intermittent “sludges” from iron sulfide contaminated crude oil that have caused negative effects on emulsion stability. At this time there remains a need for an enhanced solids removal agent or demulsifier that can promote partitioning of inorganic particulate, such as iron sulfide, from an emulsion phase  
5 to a water phase. This is essential to increase the lifetime of process equipment downstream of the desalter in a refinery, to ensure compliance with environmental regulations in streams processed by refinery waste water treatment plants and to enhance profitability.

Various methods have been used in an attempt to minimize the negative effect of  
10 entrained inorganics in the refining of crude oil. U.S. Pat. Nos. 4,778,589 and 4,789,463 disclose the use of hydroxycarboxylic acids as chemical aids for metals removal in refinery desalting processes. U.S. Pat. No. 4,833,109 to Reynolds discloses the use of dibasic carboxylic acids, particularly oxalic acid, for the removal of divalent metals, including calcium and iron. Wash water addition of hydroxyacids for removing metals  
15 during desalting processes is taught in U.S. Pat. Nos. 7,497,943, 4,778,589 and 4,789,463. U.S. Pat. No. 5,271,863 teaches the use of a Mannich reaction product to extract soluble iron and other divalent metal naphthenate complexes from crude oils. U.S. Pat. Nos. 5,114,566 and 4,992,210 teach the removal of corrosive contaminants from crude oil by adding a composition including certain organic amines having a pKb from 2 to 6 and  
20 potassium hydroxide to the desalter wash water. The composition is stated to effectively remove chlorides from the crude oil at the desalter. U.S. Pat. No. 5,078,858 suggests the addition of an oxalic or citric acid chelant to the desalter wash water. Likewise, U.S. Pat. No. 4,992,164 also suggests the addition of a chelant, particularly nitrilotriacetic acid, to desalter wash water. U.S. Pat. No. 5,256,304 is directed to the addition of a polymeric  
25 tannin material to oily waste water to demulsify oil and flocculate metal ions. U.S. Pat. No. 5,080,779 teaches the use of a chelant in a two stage desalter process for the removal of iron. Other methods involve the use of increased concentrations of emulsion breakers (aka demulsifiers).

While the methods referenced above have added technical knowledge to the art;  
30 in practice they have had limited success. In addition, some methods for removing metals and contaminants result in entrained oil in water that can negatively impact the waste water treatment plant and result in large quantities of slop oil that must be reprocessed. In addition, the various methods are not effective at removing heavy metals such as nickel

and vanadium that are organometallically complexed. These inefficiencies indicate that improved methods for the removal of particulates, including metals, from petroleum oil sources are needed.

Peroxyacids, particularly peracetic acid, have been employed in the oil and gas industry as oilfield antimicrobials in water treatment applications. See for example U.S. Pat. Nos. 2010/0160449 and 7,156,178. In addition, US. Pat. No 9,242,879 discloses their use for treatment of drilling fluids, frac fluids, flowback water and disposal water. Application of peroxyacids in the area of commercial well drilling operations have been limited to use as biocides in aqueous systems. Compared to other commercially available biocides, use of peracetic acid has a small environmental footprint, due in part to its decomposition into innocuous components (i.e., acetic acid, oxygen, carbon dioxide and water). There is a lack of teaching to suggest use of the biocidal applications to enhance particulate (including soluble and particulate metal complexes) and/or heavy metal removal from petroleum oil and refinery streams.

Accordingly, it is an object herein to identify chemical solutions to remove metals from petroleum oil sources. In addition, a further objective of the invention is to develop methods for solids stabilized emulsion control. There have been multiple studies that demonstrate adsorption of surface-modifying components in crude oil to fine particulate, resulting in increased interfacial activity. Increased emulsion stability and viscosity occurs as the concentration of surface-active material at an interface builds. Herein is a disclosure on a mechanism to prevent this phenomenon. Minimizing the concentration of particulate content in crude oil should ultimately facilitate better salt removal and dehydrating efficiency during emulsion resolution processes. Therefore, the peroxyacid formulations can also be considered emulsion breakers in their own right.

A further objective of the invention is to develop methods for removal of organometallic complexes such as porphyrinic iron, nickel or vanadium or calcium naphthenates. These organometallic compounds are not readily removed by normal desalting practices and can cause coker furnace fouling, finished products outside of specification and deactivation of hydroprocessing catalysts.

Other objects, advantages and features of the present invention will become apparent from the following description in conjunction with the accompanying Examples.

**BRIEF SUMMARY OF THE INVENTION**

The present disclosure is related to the use of peroxyacids compositions and methods of employing peroxyacids for removal of metals and particulate contained in petroleum oil, crude oil, slop oil, and other hydrocarbon streams in various refinery applications. The use of peroxyacid compositions and methods of employing them in various petroleum oil and refinery streams overcomes a significant need in the art for improved methods for removing particulate iron sulfide and zinc sulfide, along with other contaminants. These and other benefits are achieved by the methods disclosed herein.

In an embodiment, a method for removing particulates in petroleum oil and/or hydrocarbon feedstocks includes the steps of: mixing petroleum oil and/or hydrocarbon feedstock with water to form an emulsion comprising a hydrocarbon phase and a water phase; adding a peroxyacid composition to the emulsion, wherein the peroxyacid causes the particulates to move from the hydrocarbon phase into the water phase; and separating the hydrocarbon phase from the water phase to remove the particulates and the peroxyacid composition from the emulsion. In an embodiment, the peroxyacid oxidizes and chelates the particulates in the emulsion, and wherein the particulates are soluble and particulate metal complexes. In an embodiment, the peroxyacid composition comprises a C1-C22 peroxyacid, a C1-C22 carboxylic acid, and hydrogen peroxide. In embodiments, the peroxyacid is at least one of peroxyformic, peroxyacetic, peroxypropionic, peroxybutanoic, peroxy-pentanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxy-nonanoic, peroxydecanoic, peroxyundecanoic, peroxydodecanoic, or the peroxyacids of their branched chain isomers, peroxy-lactic, peroxy-maleic, peroxy-ascorbic, peroxy-hydroxyacetic, peroxy-oxalic, peroxy-malonic, peroxy-succinic, peroxy-glutaric, peroxy-adipic, peroxy-pimelic and peroxy-suberic acid. In embodiments, at least 100 ppm of the peroxyacid is added to the emulsion, or up to about 10,000 ppm of the peroxyacid is added to the emulsion. In embodiments, at least one additional agent that is a solvent, a corrosion inhibitor, an emulsion breaker or demulsifier, a scale inhibitor, metal chelant, and/or wetting agents is added to the emulsion with the peroxyacid composition. In additional embodiments, the mixture of petroleum oil and/or hydrocarbon feedstock in water is resolved in an electrostatic desalting unit. In additional embodiments, the methods further include adding an effective amount of an emulsion breaker or demulsifier to aid in the separation of the oil from the water phase containing the particulates. In still

additional embodiments, the methods further include settling the petroleum oil and/or hydrocarbon feedstock in a tank to enable the water, peroxyacid composition and particulates to settle on the bottom thereof from the petroleum oil and/or hydrocarbon feedstock. In embodiments, the petroleum oil and/or hydrocarbon feedstock is a produced crude oil and is obtained from a pipeline that directs a flow of produced crude oil. In embodiments, the petroleum oil and/or hydrocarbon feedstock once separated from the water phase does not contain any peroxyacid composition. In embodiments, the petroleum oil and/or hydrocarbon feedstock comprise petroleum oil, crude oil, slop oil, and other hydrocarbon streams from a refinery application. In any of the embodiments, the method can exclude the use of phosphoric or phosphorus acids. In an embodiment, a crude oil emulsion treatment consists of: crude oil; a peroxyacid composition for transferring metals and particulates from a hydrocarbon phase to a water phase; and a source of water. In embodiments, the treated crude oil emulsion further comprises at least one additional component that is a solvent, a corrosion inhibitor, an emulsion breaker or demulsifier, a scale inhibitor, metal chelant, and/or wetting agents.

In an embodiment, an emulsion treatment consists of: petroleum oil, crude oil, slop oil, or another hydrocarbon stream in a refinery application; a peroxyacid composition for transferring metals and particulates from a hydrocarbon phase to a water phase; and a source of water. In embodiments, the treated emulsion further comprises at least one additional component that is a solvent, a corrosion inhibitor, an emulsion breaker or demulsifier, a scale inhibitor, metal chelant, and/or wetting agents.

While multiple embodiments are disclosed, still other embodiments of the present invention will become apparent to those skilled in the art from the following detailed description, which shows and describes illustrative embodiments of the invention. Accordingly, the detailed description and its Examples are to be regarded as illustrative in nature and not restrictive.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

5           FIG. 1 shows a general diagram of a desalting process.

          FIG. 2 shows a graph of iron removal by peracetic acid, sodium gluconate or combinations thereof in both the hydrocarbon and water phases.

          FIG. 3 shows a graph of nickel removal by peracetic acid, sodium gluconate or combinations thereof in both the hydrocarbon and water phases.

10           FIG. 4 shows a graph of zinc removal by peracetic acid, sodium gluconate or combinations thereof in both the hydrocarbon and water phases.

          FIG. 5 shows a graph of iron removal by peracetic acid, sodium gluconate or combinations thereof in both the hydrocarbon and water phases.

          FIG. 6 shows a graph of zinc removal by peracetic acid, sodium gluconate or  
15 combinations thereof in both the hydrocarbon and water phases.

          FIG. 7 is a graph showing iron removal in a resolved water phase by various peroxycarboxylic and carboxylic acids.

          FIG. 8 is a graph showing nickel and zinc removal in a resolved water phase by various chemistries.

20           FIG. 9 is a graph showing the amount (ppm) of filterable solids that remained on the top oil fraction after emulsion resolution using various chemistries.

          FIG. 10 is a color photograph of four samples after centrifugation showing the resulting resolved emulsions of EC2111A and EC6779A samples at 1000 ppm and 5000 ppm.

25           While the above-identified figures set forth several embodiments, other embodiments are also contemplated, as noted in the discussion. In all cases, this disclosure presents the invention by way of representation and not limitation. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of the principles of the invention.

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**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

The present invention relates to the methods and application of peroxyacid compositions for particulate and metal removal for improving or enhancing downstream processes for petroleum oil and refinery hydrocarbon feedstocks and streams. The methods of using peroxyacid compositions have many advantages over conventional demetallization technologies. For example, the methods can take place before, after or simultaneous with a desalting step. The effective removal of metals and particulates before a desalting process can significantly minimize the effects of these contaminants on the crude unit and further downstream operations. Having metals and particulates removed before a desalting step then promotes more efficient desalting as well. Benefits can include reduced crude unit corrosion, crude system fouling, energy costs and desalting process demarks, and finished product contamination.

The embodiments of this invention are not limited to particular methods or peroxyacid compositions, which can vary and are understood by skilled artisans. It is to be further understood that all terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting in any manner or scope. For example, as used in this specification and the appended claims, the singular forms "a," "an" and "the" can include plural referents unless the content clearly indicates otherwise. Further, all units, prefixes, and symbols may be denoted in its SI accepted form.

Numeric ranges recited within the specification are inclusive of the numbers defining the range and include each integer within the defined range. Throughout this disclosure, various aspects of this invention are presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges, fractions, and individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6, etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6, and decimals and fractions, for example, 1.2, 3.8, 1½, and 4¾. This applies regardless of the breadth of the range.

So that the present invention may be more readily understood, certain terms are first defined. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention pertain. Many methods and materials similar, modified, or equivalent to those described herein can be used in the practice of the embodiments of the present invention without undue experimentation. The preferred materials and methods are described herein. In describing and claiming the embodiments of the present invention, the following terminology will be used in accordance with the definitions set out below.

10       The term "about," as used herein, refers to variation in the numerical quantity that can occur, for example, through typical measuring techniques and equipment, with respect to any quantifiable variable, including, but not limited to, mass, volume, time, distance, wave length, frequency, voltage, current, and electromagnetic field. Further, given solid and liquid handling procedures used in the real world, there is certain  
15       inadvertent error and variation that is likely through differences in the manufacture, source, or purity of the ingredients used to make the compositions or carry out the methods and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. The term "about" also encompasses these variations. Whether or not modified  
20       by the term "about," the claims include equivalents to the quantities.

      The methods and compositions of the present invention may comprise, consist essentially of, or consist of the components and ingredients of the present invention as well as other ingredients described herein. As used herein, "consisting essentially of" means that the methods, systems, apparatuses and compositions may include additional  
25       steps, components or ingredients, but only if the additional steps, components or ingredients do not materially alter the basic and novel characteristics of the claimed methods, systems, apparatuses, and compositions.

      The term "actives" or "percent actives" or "percent by weight actives" or "actives concentration" are used interchangeably herein and refers to the concentration of those  
30       ingredients involved expressed as a percentage minus inert ingredients such as water or salts.

      As used herein, the terms "preferred" and "preferably" refer to embodiments that may afford certain benefits, under certain circumstances. However, other embodiments

may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the invention.

As used herein, the term "waters" includes water in industrial and/or energy service applications. Waters in industrial and/or energy service applications include for example: aquifer water, river water, sea water, produced water, fresh water, water for injection, secondary flooding water, hot water or feedwater, ethanol/bio-fuels process waters, pretreatment and utility waters, membrane system liquids, ion-exchange bed liquids, water used in the process/manufacture of paper, ceiling tiles, fiber board, microelectronics, E-coat liquids, electrodeposition liquids, process cleaning liquids, oil exploration services liquids, oil well completion fluids, oil well workover fluids, drilling additive fluids, oil fracturing fluids, oil and gas wells, flowline water systems, natural gas water systems, or the like.

The term "weight percent," "wt. %," "wt-%," "percent by weight," "% by weight," and variations thereof, as used herein, refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100.

#### *Peroxyacid Compositions*

The methods employ at least one peroxyacid or a peroxyacid composition. Without being limited to a particular mechanism, peroxyacids and peroxyacid compositions are able to increase the hydrophilicity of particulate materials (including soluble and particulate metal complexes) in petroleum oil and refinery streams to enhance their removal from the oil/water emulsions. This beneficially allows the acid to oxidize and chelate organometallic complexes and metal-based particulates, which is distinct from use of other acids (i.e. acetic, phosphoric, or phosphorus acids which are excluded from the peroxyacids and peroxyacid compositions disclosed herein) which are only able to chelate reactive metal complexes. The approximate amount of peroxyacid required to achieve the desired amount of metal or particulate removal from an oil stream can be determined by one skilled in the art by taking into account characteristics of the stream being treated. In an aspect, the concentration of peroxyacid sufficient to demetallize a petroleum oil or refinery stream can range from 1 ppm to 10,000 ppm, between about 1,000 ppm and about 5,000 ppm, or ranges there between. In an aspect, the concentration of peroxyacid sufficient to demetallize a petroleum oil or refinery stream can be at least

about 100 ppm, at least about 1,000 ppm, at least about 2,000 ppm, at least about 3,000 ppm, at least about 4,000 ppm, at least about 5,000 ppm, at least about 6,000 ppm, at least about 7,000 ppm, at least about 8,000 ppm, at least about 9,000 ppm, at least about 10,000 ppm, or ranges there between.

5           Suitable peroxyacids include both organic and inorganic peroxyacids as set forth herein. Organic peroxyacids, include for example peroxycarboxylic acids that generally have the formula  $\text{RCO}_3\text{H}$ , where, for example, R is defined as an alkyl, alkenyl, alkyne, acyclic, alicyclic group, aryl, arylalkyl, cycloalkyl, aromatic, heteroaryl, heterocyclic group, or hydrogen. The R-group can be saturated or unsaturated as well as substituted or  
10           unsubstituted. Peroxyacids can be made, for example, by the direct action of an oxidizing agent on a carboxylic acid, by auto-oxidation of aldehydes, or from acid chlorides, and hydrides, or carboxylic anhydrides with hydrogen or sodium peroxide.

          Any suitable  $\text{C}_1\text{-C}_{26}$  peroxyacid, such as a peroxycarboxylic acid can be used. In some embodiments, the  $\text{C}_1\text{-C}_{26}$  percarboxylic acid is a  $\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4, \text{C}_5, \text{C}_6, \text{C}_7, \text{C}_8, \text{C}_9, \text{C}_{10},$   
15            $\text{C}_{11}, \text{C}_{12}, \text{C}_{13}, \text{C}_{14}, \text{C}_{15}, \text{C}_{16}, \text{C}_{17}, \text{C}_{18}, \text{C}_{19}, \text{C}_{20}, \text{C}_{21}, \text{C}_{22}, \text{C}_{23}, \text{C}_{24}, \text{C}_{25},$  and/or  $\text{C}_{26}$  percarboxylic acid. In some embodiments, a  $\text{C}_1\text{-C}_{22}$  peroxyacid is preferred, or combinations thereof.

          Peroxyacids may include short chain and/or medium chain peroxyacids. As used herein, a "short chain peracid" refers to a peroxyacid having a carbon chain between 1 and 4 carbons. Short chain peracids have the benefit of often being highly miscible in  
20           water at  $25^\circ\text{C}$ . Examples of short chain carboxylic acids include formic acid, acetic acid, propionic acid, and butyric acid. Peroxyacetic (or peracetic) acid is a peroxyacid having the formula:  $\text{CH}_3\text{COOOH}$ . Generally, peroxyacetic acid is a liquid having an acrid odor at higher concentrations and is freely soluble in water, alcohol, ether, and sulfuric acid. Peroxyacetic acid can be prepared through any number of methods known to those of  
25           skill in the art including preparation from acetaldehyde and oxygen in the presence of cobalt acetate. A solution of peroxyacetic acid can be obtained by combining acetic acid with hydrogen peroxide. In a preferred embodiment, the compositions of the invention employ a  $\text{C}_1$  to  $\text{C}_4$  peroxyacid.

          As used herein, the phrase "medium chain peracid" refers to a peroxyacid having  
30           a carbon chain between 5 and 22 carbons in length. Further as used herein, the phrase "medium chain carboxylic acid" can refer to a carboxylic acid that has a critical micellization concentration greater than 1 mM in aqueous buffers at neutral pH. It is also common for medium chain carboxylic acids to have an unpleasant odor. Medium chain

carboxylic acids exclude carboxylic acids that are infinitely soluble or miscible with water at 20°C. Medium chain carboxylic acids include carboxylic acids with boiling points (at 760 mm Hg pressure) of 180 to 300° C. In an embodiment, medium chain carboxylic acids include carboxylic acids with boiling points (at 760 mm Hg pressure) of 200 to 300°  
5 C. In an embodiment, 20 medium chain carboxylic acids include those with solubility in water of less than 1 g/L at 25° C. Examples of medium chain carboxylic acids include pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, and dodecanoic acid.

Peroxyacids useful in the methods described herein include meta-  
10 chloroperoxybenzoic, peroxyformic, peroxyacetic, peroxypropionic, peroxybutanoic, peroxy-pentanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxy-nonanoic, peroxydecanoic, peroxyundecanoic, peroxydodecanoic, or the peroxyacids of their branched chain isomers, peroxy-lactic, peroxy-maleic, peroxy-ascorbic, peroxy-hydroxyacetic, peroxy-oxalic, meta-chloroperoxybenzoic, peroxy-malonic,  
15 peroxy-succinic, peroxy-glutaric, peroxy-adipic, peroxy-pimelic and peroxy-subric acid and mixtures thereof. Inorganic peroxyacids such as peroxy-monosulfuric acid (Caro's acid) are not excluded from the peroxyacid and/or peroxyacid compositions.

In some embodiments more than one peroxyacid can be employed. For example, in some embodiments, the composition includes one or more C1 to C4 peroxyacids and  
20 one or more C5 to C22 peroxyacids. In one aspect of the invention the ratio of short chain peroxyacid to medium chain peroxyacid can be about 1:1 to about 10:1.

As referred to herein, a peroxyacid composition also includes an organic acid (i.e. corresponding carboxylic acid) and an oxidizing agent. In various aspects, the peroxyacid composition can be formed by an organic acid and an oxidizing agent. The compositions  
25 can be pre-formed. In other aspects, peroxyacid compositions may be generated in situ. Additional description of exemplary in situ methods for peroxyacids is provided for example in U.S. Patent Nos. 9,845,290, 9,518,013, 8,846,107 and 8,877,254, which are herein incorporated by reference in its entirety.

#### *Oxidizing Agent*

30 The peroxyacid compositions may also include an oxidizing agent. Most often the oxidizing agent is hydrogen peroxide. Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, provides the advantages of having a high ratio of active oxygen because of its low molecular weight (34.014 g/mole) and by being compatible with numerous substances that can be treated by

methods of the invention because it is a weakly acidic, clear, and colorless liquid. Another advantage of hydrogen peroxide is that it decomposes into innocuous water and oxygen.

The peroxyacid compositions can include any desired ratio of hydrogen peroxide. In some embodiments, the hydrogen peroxide in the percarboxylic acid composition has a concentration from about 0.5 wt-% to about 25 wt-%, preferably from about 0.5 wt-% to about 10wt-%. In other embodiments, the hydrogen peroxide has a concentration from about 1 wt-% to about 2 wt-%. In still other embodiments, the hydrogen peroxide has a concentration at about 0.5 wt-%, 1 wt-%, 2 wt-%, 3 wt-%, 4 wt-%, 5 wt-%, 6 wt-%, 7 wt-%, 8 wt-%, 9 wt-%, or 10 wt-%. In yet other embodiments, the hydrogen peroxide has a concentration at about 1 wt-%, 1.1 wt-%, 1.2 wt-%, 1.3 wt-%, 1.4 wt-%, 1.5 wt-%, 1.6 wt-%, 1.7 wt-%, 1.8 wt-%, 1.9 wt-%, 2 wt-%, 2.1 wt-%, 2.2 wt-%, 2.3 wt-%, 2.4 wt-%, 2.5 wt-%, 2.6 wt-%, 2.7 wt-%, 2.8 wt-%, 2.9 wt-%, 3 wt-%, 3.1 wt-%, 3.2 wt-%, 3.3 wt-%, 3.4 wt-%, 3.5 wt-%, 3.6 wt-%, 3.7 wt-%, 3.8 wt-%, 3.9 wt-%, or 4 wt-%.

Additional oxidizing agents include for example, the following types of compounds or sources of these compounds, or alkali metal salts including these types of compounds, or forming an adduct therewith: hydrogen peroxide, urea-hydrogen peroxide complexes or hydrogen peroxide donors of: group 1 (IA) oxidizing agents, for example lithium peroxide, sodium peroxide; group 2 (IIA) oxidizing agents, for example magnesium peroxide, calcium peroxide, strontium peroxide, barium peroxide; group 12 (IIB) oxidizing agents, for example zinc peroxide; group 13 (IIIA) oxidizing agents, for example boron compounds, such as perborates, for example sodium perborate hexahydrate of the formula  $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$  (also called sodium perborate tetrahydrate); sodium peroxyborate tetrahydrate of the formula  $\text{Na}_2\text{B}_2(\text{O}_2)_2[(\text{OH})_4] \cdot 4\text{H}_2\text{O}$  (also called sodium perborate trihydrate); sodium peroxyborate of the formula  $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4]$  (also called sodium perborate monohydrate); group 14 (IVA) oxidizing agents, for example persilicates and peroxycarbonates, which are also called percarbonates, such as persilicates or peroxycarbonates of alkali metals; group 15 (VA) oxidizing agents, for example peroxynitrous acid and its salts; peroxyphosphoric acids and their salts, for example, perphosphates; group 16 (VIA) oxidizing agents, for example peroxyulfuric acids and their salts, such as peroxymonosulfuric and peroxydisulfuric acids, and their salts, such as persulfates, for example, sodium persulfate; and group VIIa oxidizing agents such as sodium periodate, potassium perchlorate. Other active inorganic

oxygen compounds can include transition metal peroxides; and other such peroxygen compounds, and mixtures thereof.

#### *Methods of Use*

Methods of using peroxyacids (or peroxyacid compositions) to treat petroleum oils and hydrocarbon feedstocks and/or streams are particularly useful for mitigating deleterious effects caused by heavy metal concentrations, emulsion stability or high particulate content. As referred to herein, the feedstocks include any hydrocarbon feedstock including for example crude oil, slop oil, heavy residua, atmospheric or vacuum residua, deasphalted oils derived from the crude oil or residua, shale oil, liquified coal and tar sand effluent, and the like and blends thereof. As used herein, "removing" the metals and/or particulates from the petroleum oil and feedstocks (namely the hydrocarbon phase) is meant to include any and all partitioning, sequestering, separating, transferring, eliminating, dividing, removing, of one or more metal and/or particulate from the hydrocarbon phase to any extent.

In a particular embodiment particulates can include inorganic fines that are naturally occurring in crude oil such as silt, clays, silicates and metal oxides. These inorganic materials may not reactive with the peroxyacids but can be removed indirectly during an emulsion resolution process treated with the additive (*vide infra*). Particulates can also include alkali metal salts, including but not limited to, calcium carbonate ( $\text{CaCO}_3$ ), calcium sulfate ( $\text{CaSO}_4$ ), iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ), and barium sulfate ( $\text{BaSO}_4$ ).

In a particular embodiment, other heavy metals can include, but are not limited to, metal sulfides, metal chlorides, organo-porphyrins or other organometallic complexes that may react with the peroxyacid. Metals suitable for removal using the process of this invention (soluble or water insoluble) include, but are not limited to those of Groups 1, 2, 4, 5, 8, and 10 of the Periodic Table. Exemplary metals include iron, zinc, nickel, vanadium, aluminum, magnesium, titanium, sodium, potassium, calcium, and silicon. The particulates can also include chloride salts, sulfur, oxides and sulfides. Particulates can also include inorganic molecules such as iron sulfide ( $\text{FeS}$ ), zinc sulfide ( $\text{ZnS}$ ) and aluminum chloride ( $\text{AlCl}_3$ ) that are naturally occurring or arise from other chemical additives or corrosion processes.

In a particular embodiment, refinery applications include, but are not limited to raw crude processing, desalting, tankage treatment and dehydration, slop oil resolution

and mitigation, FCC desalter performance enhancement, and waste water contaminate removal and processing.

The methods of employing peroxyacids to remove fine particulates and metals from petroleum oils and refinery feedstocks includes applying or adding a peroxyacid to a wash water source, a petroleum oil and/or hydrocarbon feedstock. As referred to herein, this includes, but is not limited to, crude oil, slop oil, and water in oil or oil in water emulsions.

The oil or feedstock to be treated should preferably be in a liquid state at the selected process conditions in order to facilitate contact between the oil and the aqueous extractant (i.e. the peroxyacid and/or water). As one skilled in the art appreciates this may be accomplished by heating the oil or by the addition of a suitable solvent, e.g. a lower boiling hydrocarbon oil, as needed. The petroleum oil or feedstock to be treated is delivered to a pipeline with a heat exchanger. In such embodiments, a water supply line connects to the flow of heated oil and is delivered with the oil.

The methods may comprise, consist of and/or consist essentially of one or more of the following steps: add water and peroxyacid to a petroleum oil or hydrocarbon feedstock; add a peroxyacid to an emulsion of oil (hydrocarbon phase) and water (aqueous / water phase); water-wet particulates; oxidize metals; chelate a metal; separate the water phase containing residual peroxyacid, water soluble metal complexes, and particulates from the hydrocarbon phase. In an embodiment, the peroxyacid can be added to an emulsion formed of a hydrocarbon phase and a water phase without further addition of water.

In another embodiment, the methods of adding a peroxyacid to the petroleum oil or feedstock may precede a desalting step. A refinery's desalting unit is designed to remove entrained water, water-soluble contaminants and oil-insoluble particulates from crude oil. Crude oil is defined here as any hydrocarbon stream entering a refinery that will be processed through the desalter. This crucial step of the refining process is necessary to extend the lifetime of process equipment downstream of the unit, render the crude oil less corrosive, protect downstream refinery equipment from fouling, and to maximize throughput. The desalter achieves this by (I) providing crude oil; (II) adding wash water to the crude oil and mixing the two phases together to form an emulsion; (III) subsequently breaking the emulsion that is formed to provide an aqueous phase and a hydrocarbon phase containing a lower concentration of salt, particulate and metals. The

resolved hydrocarbon phase is commonly drawn off the top of the unit and sent to a fractionator tower. The water phase containing water-soluble metal salt compounds and sediment is discharged out the bottom of the unit and sent to a waste water treatment plant for processing. A general schematic of this process is given in FIG. 1. Desalting is  
5 traditionally enhanced by application of a high voltage electric field, heat, and by the addition of chemical additives such as emulsion breakers, solids-removal agents, and coagulants.

When effective desalting is achieved, entrained water in the crude oil will coalesce with the wash water and gravity settle to the bottom of the unit. This process is used to  
10 remove water-soluble salts such as sodium chloride, allow sediment to gravity settle, and to “water-wet” particulate. These three benefits are further elaborated on in the following discussion:

*Benefit of Removal of Residual Salts.* Water soluble salts in crude oil are typically chloride, sulfate or carbonate salts of sodium, magnesium, or calcium. If the salts are not  
15 effectively removed to the water phase, scale may result. This will reduce throughput and potentially increase operating costs. In addition, under the process conditions downstream of the desalter the salts will hydrolyze to form their acid analog, which will accelerate corrosion rates in the process vessels downstream of the unit and compromise their structural integrity.

*Benefits of Removal of Sediment.* Sediment is largely composed of naturally occurring materials, such as silicas, clays, asphaltenes, and metal oxides, resulting from the geologic formation from which the crude oil was extracted or from corrosion. This material may gravity settle in the desalter if the particle size of the sediment and conditions within the unit (emulsion viscosity, crude oil retention times etc.) are  
20 favorable. Effective removal of this water-insoluble material will increase throughput by diminishing fouling rates and will increase profitability for the refiner by decreasing the frequency at which heat exchangers must be cleaned.

*Benefits of Removal of Fine Particulate.* Fine particulate, also known as suspended solids, are hydrocarbon and water insoluble inorganics that are too small to  
30 gravity settle in the desalter. These inorganics are largely introduced into crude oil from the geological formation (sand, silt, alkali metal salts, etc.), from corrosion processes (FeS) or from upstream additives (metal based H<sub>2</sub>S scavengers, aluminum-based coagulants, etc.). When suspended in a hydrocarbon phase, particulate can lead to

operational challenges. These challenges include plugged filters, low grade coke quality, increased fouling in process equipment, and shortened lifetime of fluid catalytic cracking (FCC) catalysts. In addition, fine particulate can act as an emulsifier and exacerbate emulsion stability at the desalter, which may lead to a decrease in desalting efficiency  
5 and/or an increase in the volume of slop oil generated.

The crude oil aforementioned and desalter emulsions may have high concentrations of metals, including iron sulfide, and the methods disclosed herein beneficially removes those metals and particulates more efficiently than in a typical desalting operation. In addition, the peroxyacid formulation may enhance overall desalter  
10 performance by promoting increased removal of salt, sediment and fine particulate from the hydrocarbon phase.

In an embodiment, the peroxyacid is provided or introduced (*e.g.* injected) into a pipe and/or tank upstream of the desalter to contact the hydrocarbon. In a further aspect, the peroxyacid is preferably injected upstream of a location where the treated feed will  
15 have adequate settling time to allow the water and hydrocarbon phases to resolve and the particulates to migrate to the water phase.

In another embodiment, the methods of adding a peroxyacid to the petroleum oil or feedstock may be before, simultaneous, or after the addition of wash water to the crude oil. The method of adding a peroxyacid may also be directly into a water phase.

20 In another embodiment, the methods may also include the step of adding an effective amount of at least one additional agent or component that is water or a solvent, a corrosion inhibitor, a demulsifier (such as an oxyalkylate), a scale inhibitor, metal chelants, wetting agents and mixtures thereof. In a preferred embodiment, the methods may also include the step of adding an effective amount of an emulsion breaker (*i.e.*  
25 demulsifier) to aid in the separation of the oil from the water phase containing the particulates.

In another embodiment, the methods of adding a peroxyacid to the petroleum oil or feedstock may precede a tankage dehydration step. This may relate to dehydration of a hydrocarbon or petroleum oil stream entering a refinery tank farm or static settling of  
30 an emulsion downstream of the desalter.

The contact time for the peroxyacid will vary depending upon the process and wash water, petroleum oil and/or hydrocarbon feedstock to be treated. Here, the peroxyacid is simply added and mixed with the oil, and then is removed along with the

water phase and particulates. In an embodiment, the amount of peroxyacid added to the petroleum oil or feedstock will depend upon the oil or feedstock to be treated. As one skilled in the art appreciates, the amount of metals (e.g. iron) or particulates in the oil or feedstock can vary significantly. For example, slop oil may have a higher concentration of metals and particulates than crude oil. In an aspect, the concentration of peroxyacid provided is between about 1 ppm and about 50,000 ppm, between about 1,000 ppm and about 30,000 ppm, between about 1,000 ppm and about 20,000 ppm, or ranges there between. In an aspect, the concentration of peroxyacid is at least about 1 ppm, at least about 1,000 ppm, at least about 2,000 ppm, at least about 3,000 ppm, at least about 4,000 ppm, at least about 5,000 ppm, at least about 6,000 ppm, at least about 7,000 ppm, at least about 8,000 ppm, at least about 9,000 ppm, at least about 10,000 ppm, or ranges there between.

In an embodiment, one or more demulsifiers are added to the crude oil or wash water. The peroxyacid may also act as a demulsifier.

In an aspect, the methods beneficially reduce the metals and particulate content in the petroleum oil or refinery stream by at least about 80%, at least about 85%, at least about 90%, at least about 95%, at least about 99%, or complete removal. As one skilled in the art will ascertain the percentage of reduction of metals and particulates will be determined by the concentration of the materials in the oil and/or hydrocarbon feedstock to be treated, along with the concentration of peroxyacid employed. In a further aspect, the reduction of the metals and particulate content is achieved without any residual peroxyacid in the petroleum oil or feedstock. In a further aspect, the methods beneficially remove the metals and particulates from the hydrocarbon phase of the emulsion with little or no additional hydrocarbon entrainment into the aqueous phase.

#### *Additional Methods of Use*

The methods of using peroxyacids and peroxyacid compositions to remove fine particulates from petroleum oils and refinery feedstocks and/or streams are also useful in various additional applications. The methods of mitigation of other metals using the peroxyacids are also useful for minimizing fouling, resolving emulsions and improving waste water quality associated with petroleum oil and refinery feedstocks. The peroxyacids can be added to the oil and feedstocks to remove metals and particulates and are effective to improve the waste water from the system due in part to its decomposition

into innocuous components (i.e., acetic acid, oxygen, CO<sub>2</sub> and H<sub>2</sub>O). Moreover, the biocidal efficacy of the peroxyacids can also improve the waste water.

The methods are also useful for enhancing coke quality via contaminate removal. Highly crystalline needle coke that can be used for anodes in the aluminum and steel industry is more valuable than fuel grade coke. The crystal structure does not form in the presence of metal contaminants. Removing metals with peroxyacids promotes a higher grade of coke.

The methods are also useful for mitigating fine particulates resulting from use of metal based H<sub>2</sub>S scavengers in aqueous and hydrocarbon streams. The methods are also useful for mitigating fine particulates resulting from Aluminum and Zinc based chemical additives. The peroxyacids added to the oil and feedstocks to remove metals and particulates beneficially remove various types of particulates from these streams, including solids imparted by the various chemical additives used in the processing of the oil.

In addition, the methods are useful for mitigation of downstream catalyst poisoning and fouling, resulting in elongation of catalyst lifetimes. The peroxyacids added to the oil and feedstocks to remove metals and particulates beneficially removes these poisons from the oil and feedstock, taking them out of the downstream product which minimizes downstream catalyst poisoning and fouling. As various metals and contaminants can poison or deactivate catalysts, it is beneficial to remove the various metals and particulates with the peroxyacids.

Still further the methods are useful for reducing bacteria in slop oil and crude tanks. In an aspect, the combination of removing bacteria, contaminants, and particulates from slop oil and crude tanks is beneficial, as these sources are known to have greater amounts of iron and would therefore benefit from treatment with the peroxyacid.

All publications and patent applications in this specification are indicative of the level of ordinary skill in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated as incorporated by reference.

**EXAMPLES**

The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of this invention. It should be understood that these Examples, while indicating certain  
5       embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the embodiments of the invention to adapt it to various uses and conditions. Thus, various modifications of the embodiments of the  
10       invention, in addition to those shown and described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims. The following materials were used in the experiments set forth in the Examples:

- EC6818A – 15% peracetic acid with 10% hydrogen peroxide in water
- 15       EC6779A - 21% peracetic acid with 3% hydrogen peroxide in water
- EC2472A – primary emulsion breaker used to promote oil-water separation
- R-3461 – 30% sodium gluconate in water
- EC2111A – glacial acetic acid
- EC2483A – malic acid
- 20       EC2580A – heavy metal removal agent (polymeric material)
- EC2345A – reverse emulsion breaker/flocculent
- CORR11540A – upstream application sodium gluconate corrosion inhibitor and deoiler

- EC9008B –anionic and non-anionic surfactant blend
- 25       The portable electric desalter (PED) screening uses an Interav Model EPPT-228 apparatus. The following test method was used:

Method for replicating refinery desalting applications were employed by preparing water-in-oil emulsions by blending a fixed volume of water and crude oil under controlled conditions. The emulsion was prepared as follows:

- 30       1.       Charge 8 prescription bottles (6 oz.) with 10 mL of deionized water. Add the metals removal agent directly to the water phase (dosage to be based on total volume of water + crude oil).

2. Gently layer raw crude oil into each prescription bottle so that the total volume of liquid is equivalent to 100 mL. Add the appropriate metals removal agent directly to the hydrocarbon phase (dosage to be based on total volume of water + crude oil).
- 5 3. Use a microliter syringe to add the appropriate amount of emulsion breaker formulation to the hydrocarbon.
4. Cap the bottles loosely to prevent over-pressurization in the heated water bath. Place the containers into a water bath and equilibrate to 90°C for at least 20 minutes. Confirm the PED heater block is set to 90°C and place the PED tubes inside.
- 10 5. After 20 minutes of heating, pour the contents of Sample #1 into the first blender jar. Attach a blender cap to prevent overflow during mixing.
6. Adjust the output voltage of the rheostat to an appropriate setting (e.g., 50 % – 100 % of full power).
7. De-gas the emulsion sample by turning the blender ON and OFF as quickly as possible. Immediately after degassing, turn ON the blender and emulsify the sample for exactly 10 seconds. Warning: Adequate de-gassing and use of the blender cap should prevent blender contents from foaming over the rim of the container.
- 15 8. Pour the contents of the blender into the first PED tube. Attach the electrode cap and tighten firmly by hand. Place the sample tube in the rack in the Sample #1 position.
- 20 9. Repeat Steps 7 – 10 for each of the remaining samples, placing Sample #2 in the second position, etc. Use a clean blender container for each sample.
- Once the emulsions are poured into glass tubes (100 ml centrifuge tubes), which are then placed into the heating block of a PED heater unit, the emulsions are resolved with the assistance of constant heating and intermittent application of an electric field. The water coalescence was performed as follows:
- 25 1. When all tubes have been blended, place them inside the heating block in the appropriate positions. Increase the set temperature of the heating block from 90°C to 120°C.
- 30 2. Place the electrode assembly cover plate over the heater block to complete the electrical connection.
3. Adjust the voltage control dial to the appropriate output voltage to apply electric fields. Electric field applications are generally ten-minutes in duration and the

applied voltage is adjustable between 0 – 4000 V. The first electric field application is normally 3000 V, but the value may vary depending on observations from previous tests.

4. Current flow to the PED tubes is detected during the electric field applications by toggling the eight individual switches located directly below the ammeter.
- 5 Upon toggling each switch the needle should briefly deflect on the ammeter and return to the rest value.

5. After the first electric field application, confirm that voltage is no longer being applied by visual inspection of the warning light. Adjust the voltage control to the zero setting and remove the electrode assembly cover plate.

- 10 6. The volume of free water (in milliliters) that has separated in each PED tube after 10 minutes have elapsed is recorded. Free water is recorded as the highest volume increment where a flashlight beam is transmitted through the PED tube. If most of the water has resolved remove the tubes from the heater block. If less than 10 mL of water is observed repeat the voltage application until all the tubes have resolved most of  
15 the added water.

7. Transfer the PED tubes to a cooling rack.

8. Once the temperature is below 90°C the tubes can be opened. Sample the water phase with glass pipettes taking care to leave behind as much oil as possible. It may be necessary to repeat the extraction.

- 20 9. Submit the water samples for analysis via ICP.

The steps permit the resolution of the emulsion to be observed as the volume of free water resolved at fixed intervals during the testing. At the end of each test the resulting water phase was collected and submitted for analysis by Inductively Coupled Plasma (ICP).

- 25 The following test method was used in the Examples for a Bottle Testing:

Bottle testing was performed to identify chemistries most effective at migrating metal content to the water phase following emulsion resolution. A known amount of a representative sample of the crude oil and 10-20 mL of distilled water were placed in a series of standard bottles. One of these samples remained untreated and was used as a  
30 reference blank while the others were treated with the evaluated chemistries. The bottles were agitated simultaneously and replaced in the water bath. At specific times the amount of separated water was observed and recorded. The times of dehydration is according to the retention time in the separations vessels of the plant. Finally, this separated water was

removed and submitted for analysis by ICP.

The methods for emulsion preparation were as follows:

1. Charge medicine bottles with 100 mL the emulsion of interest.
2. Determine the relative amount of water in each emulsion by conducting a  
5 BS&W test per ASTM D-4007.
3. Use a microliter syringe to add the appropriate amount of emulsion  
breaker formulation to the emulsion.
4. Use a microliter syringe to add the appropriate amount of metals removal  
agent to the emulsion
- 10 5. Cap the bottles and shake all the samples simultaneously on a mechanical  
shaker.
6. If the emulsion requires heat for treatment, place the bottles in a water  
bath at the system temperature. Carefully loosen the caps on the bottles before placing in  
the water bath.
- 15 7. Observe and record the water drop, interface and water quality observed  
in each bottle. When most of the water has resolved sample it with a glass pipette, taking  
care to leave as much oil behind as possible.
8. Sample the water again if necessary, to remove as much oil as possible.
9. Submit the water samples for analysis by ICP.

20

#### EXAMPLE 1

Testing was conducted using the Portable Electric Desalter Screening methods to  
assess whether peracetic acid, sodium gluconate or combinations of the two additives  
could effectively migrate iron containing material from a crude oil fraction into a water  
25 phase. Metal content of a heavy crude oil sample, as reported by ICP, is shown in Table  
1.

TABLE 1

| <b>Metal</b>    | <b>Total (ppm)</b> | <b>Soluble</b> |
|-----------------|--------------------|----------------|
| Aluminum (Al)   | 4.0                | 0.3            |
| Barium (Ba)     | 2.0                | 0.1            |
| Calcium (Ca)    | 14.5               | 2.9            |
| Chromium (Cr)   | 0.2                | 0.1            |
| Cobalt (Co)     | 0.4                | 0.4            |
| Copper (Cu)     | 1.2                | 0.2            |
| Iron (Fe)       | 40.3               | 4.5            |
| Magnesium (Mg)  | 3.1                | 0.8            |
| Manganese (Mn)  | 0.7                | 0.2            |
| Molybdenum (Mo) | 0.6                | 0.4            |
| Nickel (Ni)     | 37.3               | 37.3           |
| Potassium (K)   | 14.1               | 2.3            |
| Sodium (Na)     | 64.2               | 8.7            |
| Strontium (Sr)  | 0.9                | 0.1            |
| Titanium (Ti)   | 0.8                | 0.3            |
| Vanadium (V)    | 165.0              | 165.0          |
| Zinc (Zn)       | 1.9                | 0.7            |

90 mL of the crude oil, 10 mL of deionized water and 50 ppm of EC2472A (emulsion breaker) were added to 160 mL medicine bottles. EC6779A (peracetic acid) or R-3461 (sodium gluconate in water) were screened. The additives were added to either the water or hydrocarbon phase at a concentration of 0, 1000, or 5000 ppm based on the total volume as specified in Table 2. The peracetic acid sample used was off-spec and reported at 16% actives. The solutions were then heated to 90°C for 30 minutes and then emulsified using 50% shear power. The resulting emulsions were transferred into PED tubes, capped, heated to 120°C and shocked continuously for 40 minutes with 4000 V. The resulting water phase was collected and submitted for ICP analysis. The partitioning of metals from the hydrocarbon phase to the water phase was analyzed. The concentration of Fe, Ni and Zn found in the water is given in Table 2.

15

TABLE 2

| Medicine Bottle | Ratio of EC6779A to R-3461 Solution | FeS Dissolver Total Dosage (ppm) | Concentration and phase the Fe dissolver was added to: | Iron (Fe, ppm) | Nickel (Ni, ppm) | Zinc (Zn, ppm) |
|-----------------|-------------------------------------|----------------------------------|--------------------------------------------------------|----------------|------------------|----------------|
| 3               | 1:1                                 | 5000                             | hydrocarbon                                            | 141            | 309              | 12.9           |
| 4               | 1:3                                 | 5000                             | hydrocarbon                                            | 105            | 71.2             | 6.98           |
| 5               | 0:1                                 | 5000                             | hydrocarbon                                            | 51.8           | 6.03             | 0.26           |
| 7               | 3:1                                 | 5000                             | water                                                  | 109            | 279              | 14.9           |
| 8               | NA                                  | 0                                |                                                        | 50.5           | 34.4             | 1.16           |
| 9               | 1:1                                 | 5000                             | water                                                  | 129            | 624              | 6.01           |
| 10              | 1:3                                 | 5000                             | water                                                  | 106            | 220              | 5.23           |
| 11              | 0:1                                 | 5000                             | water                                                  | 57.3           | 140              | 0.63           |
| 12              | 1:0                                 | 1000                             | hydrocarbon                                            | 88.4           | 152              | 3.32           |
| 13              | 3:1                                 | 1000                             | hydrocarbon                                            | 79.1           | 45.5             | 2.27           |
| 14              | 1:1                                 | 1000                             | hydrocarbon                                            | 77.3           | 178              | 3.01           |
| 15              | 1:3                                 | 1000                             | hydrocarbon                                            | 64             | 130              | 1.12           |
| 16              | NA                                  | 0                                |                                                        | 11.6           | 0.69             | <0.25          |
| 17              | 0:1                                 | 1000                             | hydrocarbon                                            | 8.05           | 56.3             | <0.25          |
| 18              | 1:0                                 | 1000                             | water                                                  | 85.1           | 139              | 4.69           |
| 19              | 3:1                                 | 1000                             | water                                                  | 80.4           | 92.6             | 3.4            |
| 20              | 1:1                                 | 1000                             | water                                                  | 68.4           | 34               | 0.98           |
| 21              | 1:3                                 | 1000                             | water                                                  | 59.8           | 27               | 0.93           |
| 22              | 0:1                                 | 1000                             | water                                                  | 18.8           | 25.7             | <0.25          |

Percent iron removal to the water phase, following addition of 0-1000 ppm of a metals removal agent, is shown in FIG. 2. The brown (hydrocarbon addition) versus blue (water addition) designations are used to define which phase the metal removal agent was charged into prior to emulsification. The blank sample, which contained no metals removal agent, had considerably less iron in the water at the conclusion of the test than the emulsions treated with EC6779A. By itself, R-3461 (sodium gluconate) was not effective at facilitating migration of iron to the hydrocarbon phase.

Migration of Fe to the water phase is shown as proportional to the overall dosage of EC6779A. 5000 ppm treats with EC6779A and 33% R-3461 solution gave upwards

of 30% iron removal. Similar observations were observed with regards to Ni and Zn removal as shown in FIG. 3 and FIG. 4, respectively.

#### EXAMPLE 2

- 5 A second test was conducted to verify reproducibility of the observed trends in Example #1. A sample of light crude oil was used and total metals analysis by ICP is given in Table 3. The concentration of iron in the sample was abnormally high. This was likely a result of corrosion of the metal container the sample was stored in.

TABLE 3

| <b>Total Metal</b> | <b>ppm</b> |
|--------------------|------------|
| Aluminum (Al)      | 5.79       |
| Barium (Ba)        | 12.3       |
| Calcium (Ca)       | 53.6       |
| Chromium (Cr)      | 0.131      |
| Cobalt (Co)        | <0.012     |
| Copper (Cu)        | 6.73       |
| Iron (Fe)          | 170        |
| Magnesium (Mg)     | 13.2       |
| Manganese (Mn)     | 2.14       |
| Molybdenum (Mo)    | 0.06       |
| Nickel (Ni)        | 1.76       |
| Potassium (K)      | 7.36       |
| Sodium (Na)        | 199        |
| Strontium (Sr)     | 1.92       |
| Titanium (Ti)      | 0.159      |
| Vanadium (V)       | 2.99       |
| Zinc (Zn)          | 10.7       |

- 10 The only modifications to the Example 1 method were as follows. The additives were added to either the water or hydrocarbon phase at a concentration of 500 ppm based on the total volume as specified in Table 4. The solutions were then heated to 90 °C for

30 minutes and then emulsified using 80% shear power. The concentration of Fe, Al, Ni, and Zn found in the water is tabulated in Table 4.

TABLE 4

| Bottle | Added to    | Ratio of EC6779A to R-3461      | Al (ppm)     | Fe (ppm) | Ni (ppm) | Zn (ppm)     |
|--------|-------------|---------------------------------|--------------|----------|----------|--------------|
| 1      | hydrocarbon | EC6779A                         | 97.8         | 93.4     | 198      | 44.3         |
| 2      | hydrocarbon | 3 part EC6779A to 1 part R-3461 | 33.5         | 138      | 210      | 47.5         |
| 3      | hydrocarbon | 1 part EC6779A to 1 part R-3461 | 3.76         | 118      | 168      | 18.7         |
| 4      | hydrocarbon | 1 part EC6779A to 3 part R-3461 | 8.97         | 102      | 82       | 13.1         |
| 5      | hydrocarbon | R-3461                          | 9.36         | 7.94     | 2.71     | 0.46         |
| 6      | water       | EC6779A                         | 18.9         | 114      | 128      | 49.2         |
| 7      | water       | 3 part EC6779A to 1 part R-3461 | 21.5         | 108      | 155      | 40.3         |
| 8      |             | blank                           | not detected | 2.28     | 4.42     | not detected |
| 9      | water       | 1 part EC6779A to 1 part R-3461 | 11.4         | 125      | 88.4     | 40           |
| 10     | water       | 1 part EC6779A to 3 part R-3461 | 5.69         | 137      | 5.62     | 11.7         |
| 11     | water       | R-3461                          | 3.56         | 10.2     | 1.15     | 0.45         |
| 12     |             | blank                           | not detected | 1.9      | 1.01     | not detected |

5

The percent iron and zinc removal results, based on the total concentration in the light crude, are broken out in FIG. 5 and FIG. 6, respectively. EC6779A was again observed to help facilitate Zn, Fe, and Al removal. Overall, there was a significant

increase in the concentration of the metals in the water phase relative to the blank or R-3461 treated emulsions.

### EXAMPLE 3

- 5 Additional testing was completed to compare metal removal achieved by EC6779A, EC6818A, EC2111A and EC2483A. Test methodology of Example 1 was followed using 25 ppm of EC2472A and a sample of light crude oil from the United States. EC6818A, EC6779A, EC2111A and EC2483A were tested at 1000 ppm each and compared to a blank. The emulsions were formed with 10% deionized water at 80%  
10 Variac power. Total metals analysis by ICP is given in shown in Table 5 and the results shown in Table 6.

TABLE 5

| <b>WTS</b>      |            |
|-----------------|------------|
| <b>metal</b>    | <b>ppm</b> |
| Aluminum (Al)   | 0.515      |
| Barium (Ba)     | 0.073      |
| Calcium (Ca)    | 4.43       |
| Chromium (Cr)   | 0.046      |
| Cobalt (Co)     | <0.012     |
| Copper (Cu)     | 0.139      |
| Iron (Fe)       | 24.5       |
| Magnesium (Mg)  | 1.18       |
| Manganese (Mn)  | 0.117      |
| Molybdenum (Mo) | <0.025     |
| Nickel (Ni)     | 3.7        |
| Potassium (K)   | 0.733      |
| Sodium (Na)     | 13.7       |
| Strontium (Sr)  | 0.084      |
| Titanium (Ti)   | 0.055      |
| Vanadium (V)    | 6.98       |
| Zinc (Zn)       | 0.538      |

TABLE 6

| Bottle | EC2472A<br>(ppm) | Additive            | Aluminum<br>(ppm) | Calcium<br>(ppm) | Iron<br>(ppm) | Nickel<br>(ppm) | Zinc<br>(ppm) |
|--------|------------------|---------------------|-------------------|------------------|---------------|-----------------|---------------|
| 1      | 25               | blank               | <0.150            | 14.5             | 3.96          | 0.238           | 0.106         |
| 2      | 25               | 1000 ppm<br>EC6779A | 17.1              | 17               | 98            | 123             | 3.36          |
| 3      | 25               | 1000 ppm<br>EC6818A | 18.6              | 34.3             | 109           | 22.4            | 14.9          |
| 4      | 25               | 1000 ppm<br>EC2111A | 14.4              | 16.9             | 46.9          | 7.56            | 0.524         |
| 5      | 25               | 1000 ppm<br>EC2483A | 14.4              | 16.9             | 46.9          | 7.56            | 0.524         |
| 6      | 25               | blank               | 1.03              | 13.2             | 7.19          | 0.951           | 0.473         |

The percent iron removal to the resolved water is shown in FIG. 7. EC6818A demonstrated the strongest performance under these conditions. EC2111A and EC2483A

did not show competitive performance to the two formulations containing the peroxy acid.

- 5 The same observation is observed with regards to Zn and Ni removal.

#### EXAMPLE 4

- Example 3 testing was repeated under the same conditions to analyze increased dosages of the chemistries and the effect of R-3461 on EC6818A and EC6779A performance. The experimental design and concentration of metals found in the resolved water is shown in Table 7.

TABLE 7

| Additive                              | Aluminum<br>(ppm) | Iron<br>(ppm) | Nickel<br>(ppm) | Zinc<br>(ppm) |
|---------------------------------------|-------------------|---------------|-----------------|---------------|
| 2500 ppm EC2111A                      | 20.8              | 27.5          | 8.23            | 2.93          |
| 2500 ppm EC2483A                      | 4.9               | 34.8          | 1.15            | 0.567         |
| blank                                 | 3.3               | 11.9          | 0.765           | 0.347         |
| 2500 ppm EC6779A                      | 15.6              | 111           | 66.5            | 3.39          |
| 5000 ppm EC6779A                      | 48.7              | 99.2          | 170             | 8.61          |
| 2500 ppm EC6779A with 2500 ppm R-3461 | 4.07              | 100           | 77.8            | 2.77          |
| 2500 ppm EC6818A                      | 5.28              | 95            | 214             | 6.52          |
| 5000 ppm EC6818A                      | 7.1               | 83.8          | 304             | 5.36          |
| 2500 ppm EC6818A with 2500 ppm R-3461 | 4.24              | 80.6          | 105             | 3.85          |
| blank                                 | 3.27              | 17.6          | 26.8            | 2             |

- 15 Additional data regarding performance is shown in Table 8.

TABLE 8

| <b>Additive</b>                       | <b>Aluminum<br/>(Al)</b> | <b>Iron<br/>(Fe)</b> | <b>Nickel<br/>(Ni)</b> | <b>Zinc<br/>(Zn)</b> |
|---------------------------------------|--------------------------|----------------------|------------------------|----------------------|
| 2500 ppm EC2111A                      | 449                      | 12                   | 25                     | 61                   |
| 2500 ppm EC2483A                      | 106                      | 16                   | 3                      | 12                   |
| blank                                 | 71                       | 5                    | 2                      | 7                    |
| 2500 ppm EC6779A                      | 337                      | 50                   | 200                    | 70                   |
| 5000 ppm EC6779A                      | 1051                     | 45                   | 511                    | 178                  |
| 2500 ppm EC6779A with 2500 ppm R-3461 | 88                       | 45                   | 234                    | 57                   |
| 2500 ppm EC6818A                      | 114                      | 43                   | 643                    | 135                  |
| 5000 ppm EC6818A                      | 153                      | 38                   | 913                    | 111                  |
| 2500 ppm EC6818A with 2500 ppm R-3461 | 91                       | 37                   | 315                    | 80                   |
| blank                                 | 71                       | 8                    | 80                     | 41                   |

The percent metals removal is substantially higher than expected based on the ICP analysis of the crude oil. In addition, the blanks show considerably different values for Zn and Ni suggesting the homogeneity of the crude oil sample may be of concern. R-3461A did not boost the peroxyacid formulations' performances demonstrating that the use of sodium gluconate is not required in combination with the peroxyacid compositions. However, again, the two peroxyacid formulations outperformed the carboxylic acids EC2111A (acetic acid) and EC2483A (malic acid) as shown in FIG. 8.

Filterable solids analysis on the top oil fraction of the resolved emulsion this testing is shown in FIG. 9 and suggest that solids removal has been effective relative to the blanks with the peroxyacid formulations.

#### EXAMPLE 5

Bottle Testing methodology was used to assess efficacy of various metal removal agents. Characterization of the emulsion band formed while processing this slate found 9300 ppm Fe, suggesting the Fe may play a role in emulsion stabilization. The crude oil (treated at the refinery with emulsion breaker) was homogenized and then 90 mL aliquots were transferred into five medicine bottles containing 10 mL of distilled water each. Three of the bottles were charged with one of the following metal removal agents at 1000

ppm: EC2111A, EC6779A or CORR11540A. The samples were emulsified using 100% shear and transferred to a heating block set to 120 °C. The emulsions were then shocked with 4000 V for 20 minutes to facilitate complete emulsion resolution. The samples were then cooled to ambient temperature. The resolved water phases were collected for analysis by ICP and the results are shown in Table 9. CORR11540A, a solution of R-3461 with a surfactant, did not show performance relative to EC2111A and EC6779A. This suggests again that the chelant is not effective in the absence of an acid.

TABLE 9

| <b>Treatment</b>      | <b>Aluminum (Al)<br/>(ppm)</b> | <b>Iron (Fe)<br/>(ppm)</b> | <b>Nickel (Ni)<br/>(ppm)</b> | <b>Zinc (Zn)<br/>(ppm)</b> |
|-----------------------|--------------------------------|----------------------------|------------------------------|----------------------------|
| Blank 1               | <0.75                          | <0.12                      | 1.13                         | <0.25                      |
| EC2111A (1000 ppm)    | 7.72                           | 3.55                       | 14.8                         | 1.66                       |
| EC6779A (1000 ppm)    | 9.86                           | 1.51                       | 7.67                         | 0.39                       |
| CORR11540A (1000 ppm) | <0.75                          | 0.97                       | 2.02                         | <0.25                      |
| Blank 2               | <0.75                          | 0.33                       | 0.46                         | <0.25                      |

10

**EXAMPLE 6**

The ability of peroxyacetic acid to remove metals from slop oil was analyzed. A sample of slop oil was received in the form of a stable emulsion. The emulsion does not resolve after prolonged periods of quiescent settling in the absence of chemical treatment. The sample received was homogenized and sampled into 100 mL aliquots. One aliquot each was treated with 1000 ppm of EC2483A or EC6779A. After 48 hours all the samples contained emulsion except those treated with EC6779A.

**EXAMPLE 7**

The ability of peroxyacetic acid to remove metals from slop oil (as a stable emulsion) was further analyzed. The emulsion does not resolve after prolonged periods of quiescent settling in the absence of chemical treatment. The sample received was homogenized and sampled into 100 mL aliquots. One aliquot each was treated with 1000 or 5000 ppm of EC2111A (acetic acid) or EC6779A (peracetic acid). The treated emulsions were stored for 24 hours. The two samples treated with EC6779A contained

1% resolved water. The samples were then centrifuged at 140 °C for 30 minutes. Pictures of the resulting resolved emulsion are provided in FIG. 10. The EC6779A samples contained yellow water and significantly more oil free solids were observed at the bottom of the tubes. ICP analysis on the top oil fraction and the resolved water phase are given in Table 10.

TABLE 10

| <b>Water Analysis</b>                            | <b>Al<br/>(ppm)</b> | <b>Ca<br/>(ppm)</b> | <b>Fe<br/>(ppm)</b> | <b>Ni<br/>(ppm)</b> | <b>V<br/>(ppm)</b> | <b>Zn<br/>(ppm)</b> | <b>pH@25°C</b>                    |
|--------------------------------------------------|---------------------|---------------------|---------------------|---------------------|--------------------|---------------------|-----------------------------------|
| 5000 ppm EC6779A                                 | 29.3                | 676                 | 281                 | 2.06                | 4.76               | 81.8                | 3                                 |
| 1000 ppm EC6779A                                 | 9.22                | 738                 | 175                 | 0.727               | 0.431              | 26.5                | 3                                 |
| 5000 ppm EC2111A                                 | 70.5                | 702                 | 191                 | 0.182               | 0.57               | 0.946               | 3                                 |
| 1000 ppm EC2111A                                 | 18.9                | 738                 | 159                 | 0.175               | 0.156              | 1.53                | 3                                 |
| <b>Hydrocarbon<br/>Skimmings</b>                 | <b>Al<br/>(ppm)</b> | <b>Ca<br/>(ppm)</b> | <b>Fe<br/>(ppm)</b> | <b>Ni<br/>(ppm)</b> | <b>V<br/>(ppm)</b> | <b>Zn<br/>(ppm)</b> | <b>Karl<br/>Fischer<br/>Water</b> |
| 5000 ppm EC6779A                                 | 101                 | 122                 | 288                 | 32.8                | 98.6               | 21                  | 0.34                              |
| 1000 ppm EC6779A                                 | 73.6                | 60.9                | 249                 | 36.8                | 114                | 23.2                | 0.48                              |
| 5000 ppm EC2111A                                 | 16.4                | 7.42                | 45.6                | 39.4                | 120                | 7.71                | 0.35                              |
| 1000 ppm EC2111A                                 | 26.4                | 23.1                | 70.8                | 38.2                | 119                | 9.43                | 0.1                               |
| Slop oil without<br>treatment                    | 234                 | 534                 | 686                 | 15                  | 44.1               | 66.1                |                                   |
| <b>%Removal of Metals<br/>to the Water Phase</b> | <b>Al (%)</b>       | <b>Ca<br/>(%)</b>   | <b>Fe (%)</b>       | <b>Ni (%)</b>       | <b>V (%)</b>       | <b>Zn<br/>(%)</b>   |                                   |
| 5000 ppm EC6779A                                 | 56                  | 149                 | 83                  | 15                  | 44                 | 44                  |                                   |
| 1000 ppm EC6779A                                 | 35                  | 150                 | 181                 | 16                  | 49                 | 21                  |                                   |
| 5000 ppm EC2111A                                 | 37                  | 133                 | 101                 | 17                  | 52                 | 4                   |                                   |
| 1000 ppm EC2111A                                 | 19                  | 143                 | 98                  | 16                  | 51                 | 5                   |                                   |

**EXAMPLE 8**

10 A gallon of a light crude oil from the Gulf Coast was collected for ICP analysis. An aliquot of this crude oil found 25 ppm Fe, 4 ppm Ni, and 1 ppm Zn. The crude oil was homogenized and then 90 mL aliquots were transferred into eight medicine bottles

containing 10 mL of distilled water each. The bottles were all charged with 25 ppm EC2472A and the metal removal agents as outlined in Table 11.

TABLE 11

| <b>Bottle</b> | <b>Additive</b>                       | <b>Filterable Solids on Top Oil Fraction (ppm)</b> |
|---------------|---------------------------------------|----------------------------------------------------|
| 1             | blank                                 | 1768                                               |
| 2             | 1000 ppm EC6779A                      | NA                                                 |
| 3             | 1000 ppm EC6818A                      | 1210                                               |
| 4             | 1000 ppm EC2111A                      | 1800                                               |
| 5             | 1000 ppm EC2483A                      | 1833                                               |
| 6             | blank                                 | 2008                                               |
| 7             | 2500 ppm EC2111A                      | 1490                                               |
| 8             | 2500 ppm EC2483A                      | 2008                                               |
| 9             | blank                                 | 1755                                               |
| 10            | 2500 ppm EC6779A                      | 1396                                               |
| 11            | 5000 ppm EC6779A                      | 1152                                               |
| 12            | 2500 ppm EC6779A with 2500 ppm R-3461 | 2071                                               |
| 13            | 2500 ppm EC6818A                      | 1501                                               |
| 14            | 5000 ppm EC6818A                      | 1588                                               |
| 15            | 2500 ppm EC6818A with R-3461          | 1872                                               |
| 16            | blank                                 | 976                                                |

5

The samples were emulsified using 80% shear and transferred to a heating block set to 120°C. The emulsions were then shocked with 3000 V for 20 minutes to facilitate complete emulsion resolution. The samples were then cooled to ambient temperature. The top oil fraction was sampled for filterable solids (right column of Table 11) and the resolved water phases were collected for analysis by ICP (Table 12).

10

TABLE 12

| Bottle | Additive                              | Aluminum (ppm) | Iron (ppm) | Nickel (ppm) | Zinc (ppm) |
|--------|---------------------------------------|----------------|------------|--------------|------------|
| 1      | blank                                 | <0.150         | 3.96       | 0.238        | 0.106      |
| 2      | 1000 ppm EC6779A                      | 17.1           | 98         | 123          | 3.36       |
| 3      | 1000 ppm EC6818A                      | 18.6           | 109        | 22.4         | 14.9       |
| 4      | 1000 ppm EC2111A                      | 14.4           | 46.9       | 7.56         | 0.524      |
| 5      | 1000 ppm EC2483A                      | 14.4           | 46.9       | 7.56         | 0.524      |
| 6      | blank                                 | 1.03           | 7.19       | 0.951        | 0.473      |
| 7      | 2500 ppm EC2111A                      | 20.8           | 27.5       | 8.23         | 2.93       |
| 8      | 2500 ppm EC2483A                      | 4.9            | 34.8       | 1.15         | 0.567      |
| 9      | blank                                 | 3.3            | 11.9       | 0.765        | 0.347      |
| 10     | 2500 ppm EC6779A                      | 15.6           | 111        | 66.5         | 3.39       |
| 11     | 5000 ppm EC6779A                      | 48.7           | 99.2       | 170          | 8.61       |
| 12     | 2500 ppm EC6779A with 2500 ppm R-3461 | 4.07           | 100        | 77.8         | 2.77       |
| 13     | 2500 ppm EC6818A                      | 5.28           | 95         | 214          | 6.52       |
| 14     | 5000 ppm EC6818A                      | 7.1            | 83.8       | 304          | 5.36       |
| 15     | 2500 ppm EC6818A with 2500 ppm R-3461 | 4.24           | 80.6       | 105          | 3.85       |
| 16     | blank                                 | 3.27           | 17.6       | 26.8         | 2          |

5 % Removal of Ni, Fe, Al and Zn is given in Table 13 and was approximated using the total metals analysis on the raw crude sample. R-3461 did not promote metals removal when coupled with the peroxyacids. EC6779A and EC6818A outperformed EC2111A and EC2483A. It is unclear which peroxyacid formulation is more effective based on this testing.

TABLE 13

| Bottle | Additive                              | % Migration from the Hydrocarbon Phase |           |             |           |
|--------|---------------------------------------|----------------------------------------|-----------|-------------|-----------|
|        |                                       | Aluminum (Al)                          | Iron (Fe) | Nickel (Ni) | Zinc (Zn) |
| 1      | blank                                 |                                        | 2         | 1           | 2         |
| 2      | 1000 ppm EC6779A                      | 369                                    | 44        | 369         | 69        |
| 3      | 1000 ppm EC6818A                      | 401                                    | 49        | 67          | 308       |
| 4      | 1000 ppm EC2111A                      | 311                                    | 21        | 23          | 11        |
| 5      | 1000 ppm EC2483A                      | 311                                    | 21        | 23          | 11        |
| 6      | blank                                 | 22                                     | 3         | 3           | 10        |
| 7      | 2500 ppm EC2111A                      | 449                                    | 12        | 25          | 61        |
| 8      | 2500 ppm EC2483A                      | 106                                    | 16        | 3           | 12        |
| 9      | blank                                 | 71                                     | 5         | 2           | 7         |
| 10     | 2500 ppm EC6779A                      | 337                                    | 50        | 200         | 70        |
| 11     | 5000 ppm EC6779A                      | 1051                                   | 45        | 511         | 178       |
| 12     | 2500 ppm EC6779A with 2500 ppm R-3461 | 88                                     | 45        | 234         | 57        |
| 13     | 2500 ppm EC6818A                      | 114                                    | 43        | 643         | 135       |
| 14     | 5000 ppm EC6818A                      | 153                                    | 38        | 913         | 111       |
| 15     | 2500 ppm EC6818A with 2500 ppm R-3461 | 91                                     | 37        | 315         | 80        |
| 16     | blank                                 | 71                                     | 8         | 80          | 41        |

The inventions being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the inventions and all such modifications are intended to be included within the scope of the following claims. The above specification provides a description of the manufacture and use of the disclosed compositions and methods. Since many

embodiments can be made without departing from the spirit and scope of the invention, the invention resides in the claims.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for  
5 performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilized for realizing the invention in diverse forms thereof.

10

What is claimed is:

1. A method for removing particulates in petroleum oil and/or hydrocarbon feedstocks which comprises the steps of:
  - 5 mixing petroleum oil and/or hydrocarbon feedstock with water to form an emulsion comprising a hydrocarbon phase and a water phase;  
adding a peroxyacid composition to the emulsion, wherein the peroxyacid causes the particulates to move from the hydrocarbon phase into the water phase; and  
separating the hydrocarbon phase from the water phase to remove the particulates and the  
10 peroxyacid composition from the emulsion.
2. The method of claim 1, wherein the peroxyacid oxidizes and chelates the particulates in the emulsion.
- 15 3. The method of any one of claims 1-2, wherein the particulates are soluble and particulate metal complexes.
4. The method of claim 3, wherein the metal complexes are organometallic complexes and metal-based particulates.
- 20 5. The method of claim 3, wherein the particulates comprise one or more of iron, zinc, nickel, vanadium, aluminum, barium, chromium, cobalt, copper, magnesium, manganese, molybdenum, strontium, titanium, sodium, potassium, calcium, and silicon.
- 25 6. The method of claim 1, wherein the particulates are one or more of chloride, sulfur, oxides, and sulfides.
7. The method of any one of claims 1-6, wherein the peroxyacid composition comprises a C1-C22 peroxyacid, a C1-C22 carboxylic acid, and hydrogen peroxide.
- 30 8. The method of claim 7, wherein the peroxyacid is at least one of peroxyformic, peroxyacetic, peroxypropionic, peroxybutanoic, peroxypanthanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxynonanoic, peroxydecanoic, peroxyundecanoic, peroxydodecanoic, or the peroxyacids of their branched chain isomers, peroxy-lactic,

peroxymaleic, peroxyascorbic, peroxyhydroxyacetic, peroxyoxalic, peroxymalonic, peroxysuccinic, peroxyglutaric, peroxyadipic, peroxy pimelic and peroxy subric acid.

9. The method of any one of claims 1-8, wherein at least 100 ppm of the peroxyacid  
5 is added to the emulsion.

10. The method of any one of claims 1-8, wherein up to about 10,000 ppm of the peroxyacid is added to the emulsion.

10 11. The method of any one of claims 1-10, wherein at least one additional agent that is a solvent, a corrosion inhibitor, an emulsion breaker or demulsifier, a scale inhibitor, metal chelant, and/or wetting agents is added to the emulsion with the peroxyacid composition.

15 12. The method of any one of claims 1-11, wherein the mixture of petroleum oil and/or hydrocarbon feedstock in water is resolved in an electrostatic desalting unit.

13. The method of any one of claims 1-12, further comprising adding an effective amount of an emulsion breaker or demulsifier to aid in the separation of the oil from the  
20 water phase containing the particulates.

14. The method of claim 13, further comprising settling the petroleum oil and/or hydrocarbon feedstock in a tank to enable the water, peroxyacid composition and particulates to settle on the bottom thereof from the petroleum oil and/or hydrocarbon  
25 feedstock.

15. The method of any one of claims 1-14, wherein the petroleum oil and/or hydrocarbon feedstock is a produced crude oil and is obtained from a pipeline that directs a flow of produced crude oil.  
30

16. The method of any one of claims 1-15, wherein the petroleum oil and/or hydrocarbon feedstock once separated from the water phase does not contain any peroxyacid composition.

17. The method of any one of claims 1-16, wherein the petroleum oil and/or hydrocarbon feedstock comprise petroleum oil, crude oil, slop oil, and other hydrocarbon streams from a refinery application.
- 5 18. The method of any one of claims 1-17, wherein the method does not include the use of phosphoric or phosphorus acids.
19. A crude oil emulsion treatment consisting of:  
crude oil;
- 10 a peroxyacid composition for transferring metals and particulates from a hydrocarbon phase to a water phase; and  
a source of water.
20. The treated crude oil emulsion of claim 19, further comprising at least one  
15 additional component that is a solvent, a corrosion inhibitor, an emulsion breaker or demulsifier, a scale inhibitor, metal chelant, and/or wetting agents.
21. An emulsion treatment consisting of:  
petroleum oil, crude oil, slop oil, or another hydrocarbon stream in a refinery application;
- 20 a peroxyacid composition for transferring metals and particulates from a hydrocarbon phase to a water phase; and  
a source of water.
22. The treated emulsion of claim 21, further comprising at least one  
25 additional component that is a solvent, a corrosion inhibitor, an emulsion breaker or demulsifier, a scale inhibitor, metal chelant, and/or wetting agents.